

APPLICATION FOR UNITED STATES LETTERS PATENT

for

APPARATUS AND METHOD FOR HEATING CATALYST FOR
START-UP OF A COMPACT FUEL PROCESSOR

by

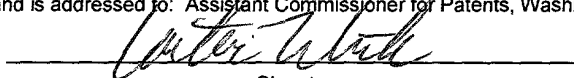
Paul Martin; T. Glenn Scott; Jennifer L. Phan; James F. Stevens; Curtis Krause

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BACKGROUND OF THE INVENTION

Fuel cells provide electricity from chemical oxidation-reduction reactions and possess significant advantages over other forms of power generation in terms of cleanliness and efficiency. Typically, fuel cells employ hydrogen as the fuel and oxygen as the oxidizing agent. The power generation is proportional to the consumption rate of the reactants.

A significant disadvantage which inhibits the wider use of fuel cells is the lack of a widespread hydrogen infrastructure. Hydrogen has a relatively low volumetric energy density and is more difficult to store and transport than the hydrocarbon fuels currently used in most power generation systems. One way to overcome this difficulty is the use of reformers to convert the hydrocarbons to a hydrogen rich gas stream which can be used as a feed for fuel cells.

Hydrocarbon-based fuels, such as natural gas, LPG, gasoline, and diesel, require conversion processes to be used as fuel sources for most fuel cells. Current art uses multi-step processes combining an initial conversion process with several clean-up processes. The initial process is most often steam reforming (SR), autothermal reforming (ATR), catalytic partial oxidation (CPOX), or non-catalytic partial oxidation (POX). The clean-up processes are usually comprised of a combination of desulfurization, high temperature water-gas shift, low temperature water-gas shift, selective CO oxidation, or selective CO methanation. Alternative processes include hydrogen selective membrane reactors and filters.

Despite the above work, there remains a need for a simple unit for converting a hydrocarbon fuel to a hydrogen rich gas stream for use with a fuel cell. A practical obstacle facing any solution to this problem is the need to start-up catalyst beds and maintain desired reaction temperatures during transient operation. The present invention addresses this need.

SUMMARY OF THE INVENTION

The present invention specifically relates to the methods and apparatus for heating a catalyst bed for start-up and for providing heat to a catalyst bed during transient operation to maintain desired reaction temperatures. Such methods and apparatus can be

1 used in a fuel processor so as to make the start-up of the fuel processor faster and easier.
2 In fuel processors there are several catalysts that may be used with the present invention,
3 including but not limited to autothermal reforming catalysts, partial oxidation catalysts,
4 steam reforming catalysts, water gas shift catalysts, preferential oxidation catalysts, and
5 sulfur absorbents, as well as with anode tailgas oxidation catalysts associated with an
6 adjoining fuel cell.

7 As embodied by the present invention an electrical heating element may directly
8 or indirectly heat the catalyst and thus rapidly obtain the desired reaction temperature
9 within the catalyst bed. The direct heating of catalyst is achieved by having direct
10 contact of the heater element with the catalyst. Indirect heating is achieved by direct
11 heating of a fluid, such as a process flow, which in turn flows through the catalyst,
12 thereby transferring heat to the catalyst. Additionally, indirect heating may be achieved
13 by placing the heating element within a sheath which is then either in direct contact with
14 the catalyst or fluid which flows through the catalyst. As is contemplated within the
15 scope of the present invention, a wide variety of catalyst forms may employ a catalyst
16 heater including pellets, extrudates, spheres, and monoliths. In one illustrative
17 embodiment of the present invention a catalyst heater in accordance with this invention
18 can be made of any resistive wire, cartridges, or rods that can be formed as outlined
19 below. A power source, such as an electric power source, provides the energy to produce
20 the heat that preheats the catalyst bed.

21 One illustrative embodiment of the present invention is a reactor in a fuel
22 processor that includes a catalyst bed, a cooling coil positioned within the catalyst bed for
23 removing excess heat during normal operation, and an electrical heating element
24 positioned within the cooling coil for heating the catalyst to a desired reaction
25 temperature during start-up and during transient operation. Such a preferred and
26 illustrative example is generally referred to in the present disclosure as sheathed heating.
27 Important illustrative advantages of this illustrative embodiment include: the provision
28 of heat to the catalyst for fast and efficient start-up, the preheating of the hydrocarbon
29 fuel feed to the fuel processor. and it provides assistance to the reactor in maintaining
30 reaction temperature during transient operation.

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1 not excluded. Thus, suitable fuels for use in the method and apparatus disclosed herein
2 include, but are not limited to hydrocarbon fuels such as natural gas, methane, ethane,
3 propane, butane, naphtha, gasoline, and diesel fuel, and alcohols such as methanol,
4 ethanol, propanol, and the like.

5 The fuel processor feeds include hydrocarbon fuel, oxygen, and water. The
6 oxygen can be in the form of air, enriched air, or substantially pure oxygen. The water
7 can be introduced as a liquid or vapor. The composition percentages of the feed
8 components are determined by the desired operating conditions, as discussed below.

9 The fuel processor effluent stream includes hydrogen and carbon dioxide and can
10 also include some water, unconverted hydrocarbons, carbon monoxide, impurities (e.g.
11 hydrogen sulfide and ammonia) and inert components (e.g., nitrogen and argon,
12 especially if air was a component of the feed stream).

13 Figure 1 depicts a general process flow diagram for a fuel processor. One of skill
14 in the art should appreciate that a certain amount of progressive order is needed in the
15 flow of the reactants through the reactors disclosed herein.

16 Process step A is an autothermal reforming process in which two reactions, partial
17 oxidation (formula I, below) and optionally also steam reforming (formula II, below), are
18 combined to convert the feed stream F into a synthesis gas containing hydrogen and
19 carbon monoxide. Formulas I and II are exemplary reaction formulas wherein methane is
20 considered as the hydrocarbon:



23 The partial oxidation reaction occurs very quickly to the complete conversion of
24 oxygen added and produces heat. The steam reforming reaction occurs slower and
25 consumes heat. A higher concentration of oxygen in the feed stream favors partial
26 oxidation whereas a higher concentration of water vapor favors steam reforming.
27 Therefore, the ratios of oxygen to hydrocarbon and water to hydrocarbon become
28 characterizing parameters. These ratios affect the operating temperature and hydrogen
29 yield.

30 The operating temperature of the autothermal reforming step can range from
31 about 550°C to about 900°C, depending on the feed conditions and the catalyst. The

1 invention uses a catalyst bed of a partial oxidation catalyst with or without a steam
 2 reforming catalyst. The catalyst may be in any form including pellets, spheres, extrudate,
 3 monoliths, and the like. Partial oxidation catalysts should be well known to those with
 4 skill in the art and are often comprised of noble metals such as platinum, palladium,
 5 rhodium, and/or ruthenium on an alumina washcoat on a monolith, extrudate, pellet or
 6 other support. Non-noble metals such as nickel or cobalt have been used. Other
 7 washcoats such as titania, zirconia, silica, and magnesia have been cited in the literature.
 8 Many additional materials such as lanthanum, cerium, and potassium have been cited in
 9 the literature as "promoters" that improve the performance of the partial oxidation
 10 catalyst.

11 Steam reforming catalysts should be known to those with skill in the art and can
 12 include nickel with amounts of cobalt or a noble metal such as platinum, palladium,
 13 rhodium, ruthenium, and/or iridium. The catalyst can be supported, for example, on
 14 magnesia, alumina, silica, zirconia, or magnesium aluminate, singly or in combination.
 15 Alternatively, the steam reforming catalyst can include nickel, preferably supported on
 16 magnesia, alumina, silica, zirconia, or magnesium aluminate, singly or in combination,
 17 promoted by an alkali metal such as potassium.

18 Process step B is a cooling step for cooling the synthesis gas stream from process
 19 step A to a temperature of from about 200°C to about 600°C, preferably from about
 20 300°C to about 500°C, and more preferably from about 375°C to about 425°C, to
 21 optimize the temperature of the synthesis gas effluent for the next step. This cooling may
 22 be achieved with heat sinks, heat pipes or heat exchangers depending upon the design
 23 specifications and the need to recover / recycle the heat content of the gas stream. One
 24 illustrative embodiment for step B is the use of a heat exchanger utilizing feed stream F
 25 as the coolant circulated through the heat exchanger. The heat exchanger can be of any
 26 suitable construction known to those with skill in the art including shell and tube, plate,
 27 spiral, etc. Alternatively, or in addition thereto, cooling step B may be accomplished by
 28 injecting additional feed components such as fuel, air or water. Water is preferred
 29 because of its ability to absorb a large amount of heat as it is vaporized to steam. The
 30 amounts of added components depend upon the degree of cooling desired and are readily
 31 determined by those with skill in the art.

Process step C is a purifying step. One of the main impurities of the hydrocarbon stream is sulfur, which is converted by the autothermal reforming step A to hydrogen sulfide. The processing core used in process step C preferably includes zinc oxide and/or other material capable of absorbing and converting hydrogen sulfide, and may include a support (e.g., monolith, extrudate, pellet etc.). Desulfurization is accomplished by converting the hydrogen sulfide to water in accordance with the following reaction formula III:



Other impurities such as chlorides can also be removed. The reaction is preferably carried out at a temperature of from about 300°C to about 500°C, and more preferably from about 375°C to about 425°C. Zinc oxide is an effective hydrogen sulfide absorbent over a wide range of temperatures from about 25°C to about 700°C and affords great flexibility for optimizing the sequence of processing steps by appropriate selection of operating temperature.

The effluent stream may then be sent to a mixing step D in which water is optionally added to the gas stream. The addition of water lowers the temperature of the reactant stream as it vaporizes and supplies more water for the water gas shift reaction of process step E (discussed below). The water vapor and other effluent stream components are mixed by being passed through a processing core of inert materials such as ceramic beads or other similar materials that effectively mix and/or assist in the vaporization of the water. Alternatively, any additional water can be introduced with feed, and the mixing step can be repositioned to provide better mixing of the oxidant gas in the CO oxidation step G disclosed below.

Process step E is a water gas shift reaction that converts carbon monoxide to carbon dioxide in accordance with formula IV:



This is an important step because carbon monoxide, in addition to being highly toxic to humans, is a poison to fuel cells. The concentration of carbon monoxide should preferably be lowered to a level that can be tolerated by fuel cells, typically below 50 ppm. Generally, the water gas shift reaction can take place at temperatures of from

1 150°C to 600°C depending on the catalyst used. Under such conditions, most of the
2 carbon monoxide in the gas stream is converted in this step.

3 Low temperature shift catalysts operate at a range of from about 150°C to about
4 300°C and include for example, copper oxide, or copper supported on other transition
5 metal oxides such as zirconia, zinc supported on transition metal oxides or refractory
6 supports such as silica, alumina, zirconia, etc., or a noble metal such as platinum,
7 rhenium, palladium, rhodium or gold on a suitable support such as silica, alumina,
8 zirconia, and the like.

9 High temperature shift catalysts are preferably operated at temperatures ranging
10 from about 300° to about 600°C and can include transition metal oxides such as ferric
11 oxide or chromic oxide, and optionally including a promoter such as copper or iron
12 silicide. Also included, as high temperature shift catalysts are supported noble metals
13 such as supported platinum, palladium and/or other platinum group members.

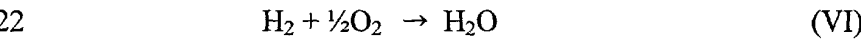
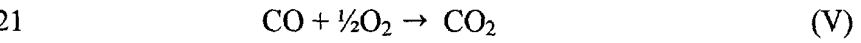
14 The processing core utilized to carry out this step can include a packed bed of
15 high temperature or low temperature shift catalyst such as described above, or a
16 combination of both high temperature and low temperature shift catalysts. The process
17 should be operated at any temperature suitable for the water gas shift reaction, preferably
18 at a temperature of from 150°C to about 400°C depending on the type of catalyst used.
19 Optionally, a cooling element such as a cooling coil may be disposed in the processing
20 core of the shift reactor to lower the reaction temperature within the packed bed of
21 catalyst. Lower temperatures favor the conversion of carbon monoxide to carbon
22 dioxide. Also, a purification processing step C can be performed between high and low
23 shift conversions by providing separate steps for high temperature and low temperature
24 shift with a desulfurization module between the high and low temperature shift steps.

25 Process step F is a cooling step performed in one illustrative embodiment by a
26 heat exchanger. The heat exchanger can be of any suitable construction including shell
27 and tube, plate, spiral, etc. Alternatively a heat pipe or other form of heat sink may be
28 utilized. The goal of the heat exchanger is to reduce the temperature of the gas stream to
29 produce an effluent having a temperature preferably in the range of from about 90°C to
30 about 150°C.

1 Oxygen is added to the process in step F. The oxygen is consumed by the
2 reactions of process step G described below. The oxygen can be in the form of air,
3 enriched air, or substantially pure oxygen. The heat exchanger may by design provide
4 mixing of the air with the hydrogen rich gas. Alternatively, the illustrative embodiment
5 of process step D may be used to perform the mixing.

6 Process step G is an oxidation step wherein almost all of the remaining carbon
7 monoxide in the effluent stream is converted to carbon dioxide. The processing is carried
8 out in the presence of a catalyst for the oxidation of carbon monoxide and may be in any
9 suitable form, such as pellets, spheres, monolith, etc. Oxidation catalysts for carbon
10 monoxide are known and typically include noble metals (e.g., platinum, palladium)
11 and/or transition metals (e.g., iron, chromium, manganese), and/or compounds of noble
12 or transition metals, particularly oxides. A preferred oxidation catalyst is platinum on an
13 alumina washcoat. The washcoat may be applied to a monolith, extrudate, pellet or other
14 support. Additional materials such as cerium or lanthanum may be added to improve
15 performance. Many other formulations have been cited in the literature with some
16 practitioners claiming superior performance from rhodium or alumina catalysts.
17 Ruthenium, palladium, gold, and other materials have been cited in the literature as being
18 active for this use.

19 Two reactions occur in process step G: the desired oxidation of carbon monoxide
20 (formula V) and the undesired oxidation of hydrogen (formula VI) as follows:



23 The preferential oxidation of carbon monoxide is favored by low temperatures. Since
24 both reactions produce heat it may be advantageous to optionally include a cooling
25 element such as a cooling coil disposed within the process. The operating temperature of
26 process is preferably kept in the range of from about 90°C to about 150°C. Process step
27 G preferably reduces the carbon monoxide level to less than 50 ppm, which is a suitable
28 level for use in fuel cells, but one of skill in the art should appreciate that the present
29 invention can be adapted to produce a hydrogen rich product with of higher and lower
30 levels of carbon monoxide.

1 The effluent exiting the fuel processor is a hydrogen rich gas containing carbon
2 dioxide and other constituents which may be present such as water, inert components
3 (e.g., nitrogen, argon), residual hydrocarbon, etc. Product gas may be used as the feed for
4 a fuel cell or for other applications where a hydrogen rich feed stream is desired.
5 Optionally, product gas may be sent on to further processing, for example, to remove the
6 carbon dioxide, water or other components.

7 In one illustrative embodiment of a fuel processor, a compact fuel processor is of
8 modular construction with individual modular units, which are separable, rearrangeable,
9 and individually replaceable. Referring to Figure 2, the compact fuel processor 100
10 includes a series of individual modules (110, 120, 130, 140, 150, 160 and 170). The
11 modular units may be used in any orientation, e.g., vertical or horizontal orientation, and
12 is adapted to be used in conjunction with a fuel cell such that the hydrogen rich product
13 gas of the reactor described herein is supplied directly to a fuel cell as a feed stream.
14 While the modules can have any cross sectional configuration, such as circular,
15 rectangular, triangular, etc., a circular cross section is preferred with the fuel processor
16 100 being of a generally tubular shape.

17 Fuel processor 100 as shown in Figure 2 effects the process diagrammatically
18 illustrated in Figure 1. Feed stream F is introduced through inlet pipe 102 and product
19 gas P is drawn off via outlet pipe 103. The apparatus 100 includes several modules that
20 may be stacked to form a modular assembly that can be modified by the replacement of
21 individual modules. Each module performs a separate operational function and is
22 generally configured as shown in Figure 2. Module 110 is the autothermal reforming
23 module corresponding to process step A of Figure 1. Module 120 is a cooling step
24 corresponding to process step B of Figure 1. In this illustrative embodiment, heat
25 exchanger 121 is shown as a general heat sink for Module 120. Module 130 is a
26 purifying module corresponding to process step C of Figure 1. Module 140 is an optional
27 mixing step corresponding to process step D of Figure 1. Feed nozzle 131 provides an
28 optional water stream feed to Module 140 to aid in driving the water gas shift reaction
29 (Equation IV) of Module 150. Module 150 is a water gas shift module corresponding to
30 process step E of Figure 1. Feed nozzle 151 provides a source for oxygen to process gas
31 for the oxidation reaction (Equation V) of Module 170. Module 150 also contains a heat

1 exchanger (not shown) positioned within or surrounding the catalyst bed so as to
 2 maintain a desired water gas shift reaction temperature. Module 160 is a cooling step
 3 corresponding to process step F of Figure 1. In this illustrative embodiment, heat
 4 exchanger 161 is shown as a general heat sink for Module 160. Module 170 is an
 5 oxidation step corresponding to process step G of Figure 1. Module 170 also contains a
 6 heat exchanger (not shown) positioned within or surrounding the catalyst bed so as to
 7 maintain a desired oxidation reaction temperature. One of skill in the art should
 8 appreciate that the process configuration described in this illustrative embodiment may
 9 vary depending on numerous factors, including but not limited to feedstock quality and
 10 required product quality.

11 The present invention specifically relates to the methods and apparatus for heating
 12 a catalyst bed for start-up and for providing heat to a catalyst bed during transient
 13 operation to maintain desired reaction temperatures. Transient operation includes but is
 14 not limited to hydrocarbon fuel feedstock changes to the fuel processor, process upsets,
 15 changes in catalyst activity, and increased or decreased volumetric throughput of feed to
 16 the fuel processor. In fuel processors such as the ones described above, there are several
 17 catalysts that may be used with the present invention, including autothermal reforming
 18 catalysts, partial oxidation catalysts, steam reforming catalysts, water gas shift catalysts,
 19 preferential oxidation catalysts, and sulfur absorbents. In these exothermic catalyst beds,
 20 heating the catalyst to reaction temperature is important for efficiently starting-up a fuel
 21 processor from a cold start. Because one envisioned use for compact fuel processors is in
 22 automotive vehicles, a solution utilizing electrical heating elements is desirable.
 23 Furthermore, transient operation is an important issue for ensuring stable hydrogen rich
 24 gas supply for a fuel cell that is fed directly from a fuel processor.

25 In general, an electrical heating element may directly or indirectly heat the
 26 catalyst. The direct heating of catalyst is achieved by having direct contact of the heater
 27 element with the catalyst. Indirect heating is achieved by direct heating of a fluid, such
 28 as a process flow, which in turn flows through the catalyst, thereby transferring heat to
 29 the catalyst. Additionally, indirect heating may be achieved by placing the heating
 30 element within a sheath which is then either in direct contact with the catalyst or fluid
 31 which flows through the catalyst. By these means, catalyst of many forms may employ

this catalyst heater including pellets, extrudates, spheres, and monoliths. The catalyst heater in accordance with this invention can be made of any resistive wire, cartridges or rods that can be formed as outlined below. A power source, such as an electric power source, provides the energy to produce the heat.

Referring now to Figure 3, face heater 300 can be utilized to provide heat to a catalyst bed face 310. The catalyst bed face is represented in this illustrative embodiment as one end of a cylindrically shaped catalyst bed. It will be appreciated by one of skill in the art that the orientation of the catalyst bed may either be vertical or horizontal in the present invention. In this illustrative embodiment, face heater 300 is an electrical heating element formed in a spiral design along the face of the catalyst bed, although other illustrative embodiments may be utilized to provide sufficient heat transfer to the catalyst bed face. By passing a small flow of reactants through the electrical heating element and catalyst bed, the exothermic reaction is initiated at the face of the catalyst bed. The heat provided by the face heater diffuses through the volume of the catalyst bed and additionally the heat of reaction produced at the catalyst bed face propagates throughout the catalyst bed thereby heating the catalyst bed for start-up. A preferred aspect of this illustrative embodiment is the use of the face heater 300 on the upstream face of the catalyst bed (i.e. the face of the catalyst bed that sees the reactor feed) such that the heat of reaction is carried into the "cold" catalyst to improve start-up efficiency of the catalyst.

Referring now to Figure 4, the electrical heating element 400 is woven through the catalyst bed 410. In this illustrative embodiment, the electrical heating element is woven through either a catalyst bed of pellets, extrudates, spheres, etc., or through a monolithic catalyst structure. The weaving design (such as a coil) may be designed for optimal heating of the catalyst bed. This illustrative embodiment provides heating from the inside of the catalyst outwards. The flowing a fluid through the catalyst during heating is optional.

Referring now to Figure 5, the electrical heating element 500 is wrapped around a monolithic catalyst structure 510. This provides heating from the outside of the catalyst towards the center. The flowing a fluid through the catalyst during heating is optional.

1 Another illustrative embodiment includes a reactor in a fuel processor that
2 includes a catalyst bed, a cooling coil positioned within the catalyst bed for removing
3 excess heat during normal operation, and an electrical heating element positioned within
4 the cooling coil for heating the catalyst to a desired reaction temperature during start-up
5 and during transient operation. This is an example of sheathed heating as described
6 above. One of skill in the art should appreciate that many advantages of this illustrative
7 embodiment are that it provides heat to the catalyst for fast and efficient start-up, it
8 preheats the hydrocarbon fuel feed to the fuel processor which may pass through the
9 cooling coil in a compact fuel processor design, and it assists the reactor in maintaining
10 reaction temperature during transient operation.

11 While the apparatus, compositions and methods of this invention have been
12 described in terms of preferred or illustrative embodiments, it will be apparent to those of
13 skill in the art that variations may be applied to the process described herein without
14 departing from the concept and scope of the invention. All such similar substitutes and
15 modifications apparent to those skilled in the art are deemed to be within the scope and
16 concept of the invention as it is set out in the following claims.

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